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(54) Title: SUPERABSORBENT POLYMERS AND PROCESS FOR PRODUCING		
(57) Abstract <p>Superabsorbent polymers of α,β-ethylenically unsaturated monomers are made by polymerizing said monomers with certain crosslinking agents, drying the polymer and heating the dried polymer at, e.g., about 165 °C to about 230 °C, for a time sufficient to produce a heat-treated polymer having a sixty minute absorbency under a 0.3 psi load of at least about 25 grams/gram. Particularly preferred superabsorbent polymers incorporate a crosslinking agent methylenebisacrylamide, bis(acrylamido)acetic acid and its salts, allyl acrylate, allylmethacrylate and difunctional monovinyl and monoallyl esters and amides, and when heat-treated provide a polymer having a sixty minute absorbency under a 0.3 psi load of at least about 30 grams/gram.</p> <p style="text-align: center;">BEST AVAILABLE COPY</p>		

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SUPERABSORBENT POLYMERS AND PROCESS FOR PRODUCING

BACKGROUND OF THE INVENTION

Water-swellaible polymers are used as constituents in sanitary materials which
5 absorb body fluids such as sanitary napkins, incontinent devices and disposable baby diapers
Examples of such polymers are disclosed in U.S. Patent Nos. 3,926,891; 4,190,562; and
4,293,609.

Various processes are known for producing absorbent polymers. For example,
U.S. Patent No. 4,833,222 teaches a process for preparing an absorbent polymer from a
10 neutralized monomer without a surface-active agent. U.S. Patent No. 4,808,637 teaches the
uniform reaction of acrylic acid, an alkali metal salt of carbonic acid, aluminum acetate, sodium
sulfate and water, preferably using microwave radiation as a heat source to initiate
polymerization

Another process comprises the steps of preparing a reaction mixture consisting
15 essentially of particular amounts of polymerizable acid group-containing monomers,
crosslinking agent and optionally free radical initiator in an aqueous medium and thereafter
polymerizing and neutralizing at least a portion of the acid functional groups.

Absorbent polymers used in personal care devices are characterized by certain
performance properties, including centrifuge capacity, absorbence under load, shear modulus,
20 and percent extractables.

The centrifuge capacity of a polymer is quotient of the weight of the 0.9 percent
saline solution retained by a swollen polymer after centrifugation to remove interstitial water
divided by the non-swollen weight. Unless otherwise indicated, centrifuge capacity values
disclosed herein are determined as described in U.S. Patent 4,286,082, the relevant portions of
25 which are incorporated herein by reference, except that an absorption time of 30 minutes
rather than 3 to 5 minutes is employed. Preferred centrifuge capacities are those greater than
about 26 grams/gram. Especially preferred centrifuge capacities are those greater than about
30 grams/gram.

Sixty minute 0.3 psi absorbance under load (AUL) refers to the ability of the polymer to swell against a pressure of 0.3 psi. Sixty minute 0.3 psi AUL reflects the ability of the polymer to absorb, e.g., when the user of a personal care device is seated. Unless otherwise indicated, sixty minute 0.3 psi AUL values disclosed herein are determined as described in European Patent Application EP 339,461-A1, the relevant portions of which are incorporated herein by reference. Preferred sixty minute 0.3 psi AUL values are those greater than about 25. Especially preferred sixty minute 0.3 psi AUL values are those greater than about 30.

Shear modulus refers to the ratio of applied stress to induced strain as the polymer is deformed. Unless otherwise indicated, modulus values disclosed herein are determined as described in U.S. Reissue Patent 32,649. Preferred shear moduli are those greater than about 40,000 dynes/cm².

In general, capacity is inversely proportional to sixty minute 0.3 psi AUL and shear modulus. One of the main goals of polymer design has been to increase the sixty minute 0.3 psi AUL of the polymer without decreasing the shear modulus or centrifuge capacity.

Further, absorbent polymers used in personal care devices should have minimal 16 hour extractables levels, i.e., soluble, uncrosslinked polymer levels. Generally, higher levels of extractables retard the transfer of liquid through an absorptive product. Unless otherwise indicated, 16 hour extractables values disclosed herein are determined as described in U.S. Reissue Patent 32,649. Preferred absorbent polymer will have a 16 hour extractables level less than about 10 percent, more preferably less than about 5 percent.

U. S. Patent No. 4,666,983 disclosed an absorbent article obtained by mixing 100 parts by weight of an absorbent resin powder having a carboxyl group with 0.001 to 10 parts by weight of a crosslinking agent, and reacting the absorbent resin powder with the crosslinking agent, typically by heating at a temperature between 90°C and 300°C to form surface crosslinked polymers. The surface crosslinked polymers are said to have improved ratios of absorption, as compared to non-surface crosslinked polymers. This process suffers the disadvantage of requiring a crosslinking agent, in addition to that present in the monomer mixture, to effect the improvement in absorptive properties.

Accordingly, those in industry would find great advantage in a process for improving the sixty minute 0.3 psi AUL of a water-swellaible polymer while simultaneously maintaining a low 16 hour extractables level, and while not significantly decreasing (if not increasing) the centrifuge capacity and shear modulus. Such a process should not require the use of a secondary surface crosslinking agent during heat treatment.

SUMMARY OF THE INVENTION

The present invention provides a process for producing a superabsorbent polymer comprising polymerizing an α,β -ethylenically unsaturated monomer in an aqueous phase in the presence of a suitable initiator and a crosslinking agent and thereafter drying the polymer at a temperature between about 100°C and about 180°C to form a dried polymer, characterized in

that the process further comprises heating the dried polymer in the absence of a surface crosslinking agent to a temperature between about 165°C and about 230°C for a time sufficient to produce a heat-treated polymer having a sixty minute 0.3 psi AUL of at least about 25 grams/gram.

- 5 In a particularly preferred embodiment, the aqueous phase will further comprise a C₁ to C₆ alkyl acrylate, whereupon the heat-treated polymer has a sixty minute 0.3 psi AUL of at least about 28 grams/gram.

In an especially preferred embodiment, the crosslinking agent will be selected from the group consisting of methylenebisacrylamide, bis(acrylamido)acetic acid and its salts,
10 allyl acrylate, allylmethacrylate and esters or amides having both a vinyl and an allyl functionality, whereupon the heat-treated polymer has a sixty minute 0.3 psi AUL of at least about 30 grams/gram.

The present invention further provides a superabsorbent polymer comprising polymerized moieties of at least one α,β -ethylenically unsaturated monomer and at least one
15 crosslinking agent, said polymer being characterized by a 60 minute 0.3 psi AUL of at least about 30 grams/gram, a centrifuge capacity of at least about 32 grams/gram, and a 16 hour extractables level less than about 4 percent.

The present invention further provides a method of using such a superabsorbent polymer, comprising retaining said polymer in conjunction with hydrophilic fibers in an
20 absorbent structure. Such absorbent structure may in turn be retained within a disposable diaper, a sanitary napkin, or an incontinence device.

The superabsorbent polymers made by the process of this invention enjoy an increased AUL, a high centrifuge capacity and modulus, and a low 16 hour extractables level.

DETAILED DESCRIPTION OF THE INVENTION

25 Suitable water-soluble α,β -ethylenically unsaturated monomers that are useful in the present invention include those monomers which are capable of conversion by aqueous solution polymerization into a water-swellaable and/or lightly crosslinked hydrophilic gel polymer. The crosslinked structure may be obtained by the copolymerization of a water-soluble monomer and a crosslinking agent possessing at least two polymerizable double bonds
30 in the molecular unit.

The water-swellaable or lightly crosslinked hydrophilic polymers that are prepared by the method of the present invention can be any of the known hydrophilic polymers which are capable of absorbing large quantities of fluids. Examples of such polymers and processes for preparing them are disclosed in U.S. Patent Nos. 3,997,484; 3,926,891; 3,935,099; 4,090,013;
35 4,093,776; 4,340,706; 4,446,261; 4,683,274; 4,459,396; 4,708,997; 4,076,663; and 4,190,562 herein incorporated by reference. Such hydrophilic polymers are prepared from water-soluble α,β -ethylenically unsaturated monomers such as monocarboxylic acids, polycarboxylic acids, acrylamide and their derivatives.

Suitable α,β -ethylenically unsaturated monomers include, for example, acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid and alkali metal salts and ammonium salts thereof; maleic acid, fumaric acid, itaconic acid, acrylamide, methacrylamide and 2-acrylamido-2-methyl-1-propane sulfonic acid and its salts. The preferred monomers include acrylic acid and methacrylic acid and their respective salt forms such as alkali metal or ammonium salts.

The water-soluble monomers useful in the present invention may be used in amounts ranging from about 10 percent to about 80 percent by weight based on the total weight of the aqueous monomer solution. Preferably, the amount ranges from about 20 percent to about 60 percent based on the total weight of the aqueous monomer solution.

Optionally, the minor amounts of other water-soluble, unsaturated monomers, such as alkyl esters of the acid monomers, e.g., methyl acrylate or methyl methacrylate may be present. In addition, certain grafting polymers, such as, for example, polyvinyl alcohol, starch and water soluble or swellable cellulose ethers may be employed to prepare products having superior properties. Such grafting polymers, when employed, are used in amounts up to about 10 weight percent based on the α,β -ethylenically unsaturated monomer. Further, it may be advantageous to include a chelating agent to remove trace metals from solution, e.g., when a metal reaction vessel is employed. One such chelating agent is VERSENEX 80 (an aqueous solution of the pentasodium salt of diethylenetriamine pentacetic acid) (Trademark of The Dow Chemical Company). Such chelating agents, when employed, are generally used in amounts between about 100 and about 2000 ppm based on the α,β -ethylenically unsaturated monomer.

It is desirable to obtain a level of conversion of monomer to polymer of at least about 95 percent conversion. The polymerization may be carried out using acid monomers that are not neutralized or that have been neutralized or partially neutralized prior to the polymerization. Neutralization is conveniently achieved by contacting the aqueous monomer with an amount of basic material sufficient to neutralize between about 20 and about 95 percent of the acid groups present in the acid monomers. Preferably, the amount of basic material will be sufficient to neutralize between about 40 percent and 85 percent, and most preferably between about 55 percent and about 75 percent of the acid groups present in the acid monomers. When pre-neutralizing the monomer solution, it is important to control the neutralization conditions so that the heat of neutralization does not cause the premature polymerization of the monomer mixture. The neutralization is advantageously carried out at temperatures below about 40°C, preferably at temperatures below about 35°C.

Compounds which are useful to neutralize the acid groups of the monomer are typically those which will sufficiently neutralize the acid groups without having a detrimental effect on the polymerization process. Such compounds include alkali metal hydroxides, alkali metal carbonates and bicarbonates. Preferably, the material used to neutralize the monomer is sodium or potassium hydroxide or sodium carbonate or potassium carbonate. In determining

the desired degree of neutralization, care must be taken to ensure that the pH of the resulting crosslinked absorbent polymer, which will be contacted with or dispersed in an aqueous fluid to be absorbed, is maintained in a range appropriate for the applications for which the polymer is intended. Alternatively, the polymerization may be carried out employing
5 unneutralized monomers and thereafter neutralizing, as is known in the art.

Conveniently, a conventional vinyl addition polymerization initiator is used in the polymerization of the water-soluble monomers and the crosslinking agent. A free radical polymerization initiator which is sufficiently soluble in the monomer solution to initiate polymerization is preferred. For example, water soluble peroxides such as potassium
10 persulfate, ammonium persulfate, sodium persulfate, and other alkali-metal persulfates, hydrogen peroxide and water soluble azo-compounds such as 2,2'-azobis (2-amidinopropane-HCL) may be used. Some of these initiators, such as hydrogen peroxide can be combined with reducing substances such as sulfites or amines to form known redox type initiators. The amount of initiator used may range from about 0.01 to about 1.0 weight percent, preferably
15 about 0.01 to about 0.5 weight percent, based on the total weight of α,β -ethylenically unsaturated monomer reactants.

The crosslinking agent is present in an amount effective to crosslink the water-soluble polymer. The preferred amount of crosslinking agent is determined by the desired degree of absorption capacity and the desired strength to retain the absorbed fluid. Typically,
20 the crosslinking agent is used in amounts ranging from about 0.0005 to about 5 parts by weight per 100 parts by weight of α,β -ethylenically unsaturated monomer used. More preferably, the amount ranges from about 0.1 to about 1 part by weight per 100 parts by weight of the α,β -ethylenically unsaturated monomer. If an amount over about 5 parts by weight of crosslinking agent per 100 parts is used, the resulting polymer has too high a crosslinking density and
25 exhibits a reduced absorption capacity and increased strength to retain the absorbed fluid. If the crosslinking agent is used in an amount less than about 0.0005 part by weight per 100 parts, the polymer has too low a crosslinking density, and when contacted with the fluid to be absorbed becomes sticky and exhibits a lower initial absorption rate.

While the crosslinking agent will typically be soluble in the aqueous solution of
30 the α,β -ethylenically unsaturated monomer, the crosslinking agent may be merely dispersible in such a solution, without negative implications. The use of such dispersing agents is disclosed in U.S. Patent No. 4,833,222, the relevant portions of which are incorporated herein by reference. Suitable dispersing agents include carboxymethyl cellulose suspending aids, methyl cellulose, hydroxypropyl cellulose, and polyvinyl alcohol. Such dispersing agents are typically provided at
35 a concentration between about 0.005 and about 0.1 weight percent, based on the total weight of α,β -ethylenically unsaturated monomer reactants.

Suitable crosslinking agents are those which, when used, increase the sixty minute 0.3 psi AUL of the polymer, without significantly decreasing (if not increasing) the centrifuge

capacity. Preferred crosslinking agents include trimethylolpropanetriacrylate, butyleneglycoldiacrylate, ethyleneglycoldimethacrylate, ethylenebisacrylamide and diallylcarbonate, methylenebisacrylamide, bis(acrylamido)acetic acid and its salts, allyl acrylate, allylmethacrylate and difunctional monovinyl and monoallyl esters and amides. Especially
5 preferred crosslinking agents include methylenebisacrylamide, bis(acrylamido)acetic acid and its salts, allyl acrylate, allylmethacrylate and, esters or amides having both a vinyl and an allyl functionality.

In a preferred embodiment for making polymers useful in the practice of this invention, an aqueous solution of the α,β -ethylenically unsaturated monomer in the partially
10 neutralized form, the crosslinking agent, the initiator and a grafting polymer substrate, if desired, is prepared.

The polymerization of the mixture may be initiated by elevating the temperature of the mixture containing the initiator or by using a redox-type initiator as described above. Generally, the temperature at which polymerization will begin ranges from about 20°C to
15 about 45°C. The temperature at which the polymerization is carried out is highly dependent on the type of monomers used and the specific initiator system employed. Preferably, the maximum temperature of polymerization ranges from about 50°C to about 100°C, most preferably from about 60°C to about 90°C. The method by which the temperature of the polymerization is controlled is not critical so long as sufficient cooling is present to remove the
20 heat which is generated during the polymerization.

After polymerization, the gel is dried in, e.g., a circulating air oven, to a moisture content less than about 10 percent, preferably less than about 5 percent, most preferably about 2 to about 5 percent, expressed on a dried polymer basis, to form a "dried polymer".

It has advantageously been discovered that when the dried polymer is further
25 heated at elevated temperatures, the sixty minute 0.3 psi AUL increases, the centrifuge capacity and the modulus do not significantly decrease (if they do not increase), and the 16 hour extractables levels remain low (if they do not decrease). Such heat treatment is preferably carried out at temperatures between about 165°C and about 230°C, more preferably between about 190°C and 210°C.

30 The time for heat treatment can best be determined empirically, with such factors as humidity within the heat treatment apparatus, water content of the dried polymer, rate of temperature elevation, and type of crosslinking agent employed affecting the time. However, it has been found that when trimethylolpropanetriacrylate, butyleneglycoldiacrylate, ethyleneglycoldimethacrylate, ethylenebisacrylamide or diallylcarbonate are used as
35 crosslinking agents, absorptive properties improve with additional heating to a point, after which further heating causes a decrease in absorptive properties. In contrast, it has been found that when methylenebisacrylamide, bis(acrylamido)acetic acid or one of its salts, allyl acrylate, allylmethacrylate, or an ester or amide having both a vinyl and an allyl functionality are used as

crosslinking agents employed, absorptive properties do not appear to degrade upon heating beyond the point at which a maximum increase in absorptive properties has occurred..

The method of heat treating is not critical; for example, forced air ovens, fluidized bed heaters, heated screw conveyors and the like may be successfully employed. If
5 desired, the heat treated polymer may be remoisturized for ease in handling.

Increases in shear modulus, sixty minute AUL, free swell capacity, and centrifuge capacity can simultaneously be obtained at lower temperatures (and at higher temperatures for shorter heating times) by incorporating pendant ester groups into the polymer. While not wishing to be bound by theory, it is believed that the incorporation of pendant ester groups
10 into the polymer increases the modulus and AUL of the polymer by facilitating the formation of inter- or intramolecular anhydride crosslinks, i.e., crosslinks wherein ester and acid functionalities combine with the release of an alcohol. While such crosslinks may be achieved by mere heating (with the release of water, rather than an alcohol), it is believed that such crosslinks are formed more easily by heating an ester with an acid group, since an alkoxy group
15 is a better leaving group than a hydrogen group.

Pendant ester groups may be incorporated into the polymer by copolymerizing acrylic acid and/or sodium acrylate with an C₁ to C₆ acrylate or a methacrylate. Preferred acrylates and methacrylates are monofunctional crosslinking agents, and include ethyl, propyl, isopropyl, butyl, and isobutyl acrylates or methacrylates. The acrylate or methacrylate will
20 preferably be soluble in the aqueous solution of the α,β -ethylenically unsaturated monomer. In the alternative, the acrylate or methacrylate will be merely dispersible in such a solution. Suitable dispersing agents and concentrations are as set forth above with respect to agents suitable to disperse the crosslinking agent. The use of dispersing agents will enable the use of larger molecular weight acrylates and methacrylates, e.g., pentyl and hexyl acrylates and
25 methacrylates.

To achieve the benefits such pendant ester groups afford, the monofunctional acrylate and/or methacrylate will preferably be provided in the range of between about 0.5 and about 10 percent, and more preferably between about 1 and about 5 percent, based on the weight of the monomer reactants.

The following examples are provided for the purpose of explanation rather than limitation. Unless otherwise indicated, sixty minute 0.3 psi AUL was measured as described in European Patent Application EP 339,461- A1; centrifuge capacity was determined as described in U.S. Patent 4,286,082 except that an absorption time of 30 minutes rather than 3 to 5 minutes was employed; and the extractables and modulus were determined as described in
30 U.S. Reissue Patent 32,649, with the relevant portions of each of the cited references being
35 incorporated herein by reference.

Example 1: General Heat Treatment for the Reduction of Extractables in 55 Percent Neutralized Polyacrylic Acid

Two-point one (2.1) grams of trimethylolpropane triacrylate, 0.2 grams of VERSENEX 80 chelating agent (available from the Dow Chemical Company), and 1.5 grams of a 5 percent aqueous solution of polyvinyl alcohol such as AIRVOL V-205, were added to 300 grams of acrylic acid. The resultant solution was neutralized to 55 percent by the addition of 121.8 grams of sodium carbonate in 792.5 grams of water and diluted to a total weight of 1168 grams with water. The neutralized solution was purged for 1 hour with nitrogen. The polymerization was initiated by adding 0.75 grams of sodium persulfate, 0.15 grams of WAKO V-50 (2,2' azobis (2-amidino-propane) dihydrochloride), 0.13 grams of a 70% aqueous solution of t-butyl hydroperoxide, and 4.5 ML of a 15% aqueous solution of sodium thiosulfate. After the reaction temperature peaked, the temperature was decreased to 60°C, which temperature was maintained an additional three hours. The gel was dried at 100°C for 6 hours and then ground through a knife grinder. Portions of the material were heated in a forced air oven at various temperatures. The analysis is set forth in the following Tables I and II.

TABLE I

16 Hour Extractables Levels
(percent) after Heating at 200°C
for Indicated Number of Minutes

Sample	0	20	40	60
1	8.7	7.6	6.5	6.1
2	7.7			5.9
3	10.2			7.1
4	11.4			7.8

TABLE II

16 Hour Extractables Levels
(percent after Heating at 150°C
for Indicated Number of Minutes

Sample	0	20	40	60
1	8.7	9.0	9.0	8.8

Example 2: The Effect of Heat Treatment at Various Degrees of Neutralization on Percent Extractables

A gel was prepared in accordance with Example 1. Various degrees of neutralization were achieved by neutralizing the monomer solution with varying amounts of sodium carbonate solution. The gel was dried and heat treated in accordance with the procedure set forth in Example 1. The degree of neutralization, and the 16 hour extractables levels of the polymer upon heating at 200°C for one hour are set forth in the following Table III.

TABLE III: 16 Hour Extractables
Levels (percent)

Sample	% Neutralized	Initial	Heat Treated
1	0	7.7	6.2
2	40	4.3	2.7
3	50	5.8	2.8

Example 3: The Effect of Heat Treatment on Absorptive Properties

Five samples of trimethylolpropanetriacrylate crosslinked Dow DRYTECH superabsorbent polymer were obtained from the Dow DRYTECH superabsorbent polymer plant in Midland, Michigan. The properties of such samples, prior to heat treatment, are set forth in Table IV. Such samples were heated at 200°C in a forced air oven for various times. Various absorptive properties, such as modulus, free swell capacity, centrifuge capacity, 5 minute 0.3 psi AUL, 60 minute 0.3 psi AUL, and 16 hour extractables levels, were measured. Free swell capacity is determined by allowing 1.0 gram of the polymer to absorb its limit of 300 grams of a 0.9 percent saline solution in 20 minutes. The excess salt solution which is not absorbed is weighed and subtracted from the original 300 grams to give the free swell capacity. Five minute 0.3 psi AUL is measured following the procedure set referenced for the measurement of sixty minute 0.3 psi AUL, excepting that the amount of fluid pickup is measured after five minutes, rather than after sixty minutes.

The data are further set forth in the following Table IV.

TABLE IV

Sample	Time at 200°C (min)	Shear Modulus (dynes/cm ²)	Free Swell Capacity (g/g)	Centrifuge Capacity (g/g)	5 min AUL (g/g)	60 Min AUL (g/g)	16 hour Extractables (%)
1	0	40,400	35.5	32.7	3.1	13.8	10.6
	8	-	-	32.4	7.4	26.1	-
	16	49,800	34.0	31.6	14.1	28.0	-
	32	49,800	34.9	30.4	15.5	26.8	-
	64	52,300	36.3	28.0	13.9	26.3	10
2	0	60,400	33.0	28.3	5.6	26.4	7.7
	8	-	-	28.6	12.6	27.7	-
	16	66,400	30.0	26.5	25.0	27.2	-
	32	72,400	30.3	25.4	18.1	26.5	-
	64	78,700	32.4	24.7	21.6	26.5	5.9
	90	75,700	28.0	-	-	-	-
3	0	-	-	43.6	2.6	7.5	-
	8	-	-	35.8	4.4	12.2	-
	16	-	-	32.9	5.5	16	-
	32	-	-	30.2	7.6	21.2	-
4	16	52,100	32.6	29.8	-	27.5	-
	32	69,700	28.1	24.8	-	24.7	-
	64	77,300	25.5	22.9	-	22.6	5.1
5	0	27,700	37.1	37.7	-	12.2	6.9
	8	35,000	36.5	37.2	-	16.1	-
	16	39,300	35.3	34.4	-	26.5	-
	32	41,400	33.4	29.4	-	26.4	-
	64	50,600	31	26.4	-	24.5	5.64
6	0	-	-	32.8	8.9	19.4	-
	8	-	-	31.2	8.9	26.0	-
	16	-	-	28.9	8.7	26.4	-
	32	-	-	27	8.4	25.7	-

This data suggests that heat treatment increases a low 60 minute 0.3 psi AUL, e.g., a 60 minute 0.3 psi AUL less than 20, to at least 25. Such heat treatments increase the modulus, and do not significantly adversely affect the free swell capacity, the centrifuge capacity, or the 5 minute 0.3 psi AUL of the polymer. This suggests that heat treatment would enable the modification of a batch of polymer which has a non-preferred low sixty minute 0.3 psi AUL, rendering it highly useful and saleable. The data further shows the tendency of heat treatment to maintain low 16 hour extractables levels, if not decrease them.

Example 4: Comparison of Different Heat Treatment Temperatures and Times on Absorptive Properties

A sample of DRYTECH™ 533 trimethylolpropanetriacrylate crosslinked superabsorbent polymer was obtained from the Dow Chemical Company (Midland, MI). The sample was heat treated at an indicated temperature for an indicated period of time. The temperatures and times of heat treatment, and the resultant properties of the heat-treated polymer, are set forth in Table V. The method utilized to determine one hour extractable levels is substantially as described in U.S. Patent Reissue No. 32,649, the relevant portions of which are incorporated herein by reference.

TABLE V

Temperature of Heat Treatment (°C)	Time of Heat treatment (minutes)	60 minute 0.3 psi AUL (g/g)	centrifuge capacity (g/g)	1 hour extractable level (%)
none	none	21.1	32.6	8.5
145	16	23.1	33.2	8.1
	32	22.7	33.2	
167	8	25.3	33.2	8.0
	16	23.8	32.5	
	32	24.4	29.4	
175	8	23.7	33.2	7.7
	16	26.0	31.7	
	32	25.7	30.9	
198	8	26.5	29.7	7.7
	16	27.3	29.2	

This data suggests that for trimethylolpropane triacrylate crosslinked polymers, heat treatment temperatures greater than about 165°C are preferred, with heat treatment temperatures greater than about 175°C being especially preferred.

Example 5: The Effect of Heat Treatment on Copolymers of Neutralized Acrylic Acid and Methyl Acrylate

To 300 grams of acrylic acid were added 2.1 grams of trimethylolpropanetriacrylate, 0.2 grams of VERSENEX 80 chelating agent (available from the Dow Chemical Company), 1.5 grams of a 5 percent aqueous solution of AIRVOL V-205 polyvinyl alcohol (available from Air Products Corporation), and 15 grams of methyl acrylate. The solution was neutralized by the addition of a solution of 121.8 grams of sodium carbonate in 792.5 grams of water. The neutralized solution was diluted to a total weight of 1168 grams with water. The diluted solution was purged for one hour with nitrogen. To initiate polymerization, 0.75 grams of sodium persulfate, 0.15 grams of WAKO V-50 azo-initiator

- (available from Pure Chemicals Inc.), 0.09 grams of a 70% aqueous solution of t-butylhydroperoxide, and a reducing agent (such as sodium thiosulfate) were added to the purged solution. After the reaction temperature peaked, the polymer was heated an additional 3 hours at 60°C to form a gel. The gel was dried at 100°C for 6 hours, and was
- 5 ground through a knife grinder. Portions of the ground material were heated in a forced air oven at various temperatures for various periods of time. The resultant data is set forth in the following Tables VI and VII.

TABLE VI

% Methyl acrylate	Time at 150°C (min)	Shear Modulus (dynes/cm ²)	Free Swell Capacity (g/g)	Centrifuge Capacity (g/g)	60 Min 0.3 psi AUL	16 hour Extractable (%)
0	0	46,800	30.0	29.2	26.6	3.76
	8	53,600	31.3	29.9	26.7	
	16	53,700	31.0	30.1	27.4	
	32	57,200	31.7	30.0	27.5	
	64	53,900	31.9	29.7	27.6	3.93
1	0	46,000	29.6	29.4	27.0	3.37
	8	49,700	31.0	30.4	27.7	
	16	50,900	31.5	30.4	27.8	
	32	52,200	31.1	30.6	28.6	
	64	55,600	30.0	30.5	28.3	3.2
5	0	44,100	32.0	31.2	26.8	3.93
	8	46,700	32.8	31.5	26.5	
	16	48,500	33.0	31.7	28.4	
	32	49,600	33.5	31.7	28.6	
	64	53,500	33.3	31.5	29.6	3.76

TABLE VII

% Methyl acrylate	Time at 200°C (min)	Shear Modulus (dynes/cm ²)	Free Swell Capacity (g/g)	Centrifuge Capacity (g/g)	60 Min AUL (g/g)	16 Hour Extractables (%)
0	0	46,800	30.0	29.2	26.6	3.76
	8	55,900	32.0	29.3	27.6	
	16	64,000	29.2	27.2	26.1	
	32	76,400	25.7	23.4	23.8	2.36
	64	87,000	23.3	20.6	21.3	
1	0	46,000	29.6	29.4	27.0	3.37
	8	56,800	31.5	30.0	28.3	
	16	62,400	29.0	27.5	26.7	
	32	79,100	27.3	23.5	24.1	2.36
	64	84,800	23.9	21.2	22.5	
5	0	44,100	32.0	31.2	26.8	3.93
	8	54,800	33.0	30.7	29.2	
	16	60,000	31.0	28.6	27.7	
	32	75,100	28.0	25.1	25.0	2.64
	64	81,600	26.5	22.2	23.3	

The data of Table VI suggests that heat treating a polymer containing methyl acrylate at 150°C and 200°C improves the absorptive properties of the polymer, providing polymers having a sixty minute 0.3 psi AUL of at least about 28.

Example 6: Heat Treatment of Polymers Prepared with Preferred Crosslinking Agents

- 25 The reactor consisted of a 2 liter glass resin reaction kettle bottom, a stainless steel agitator assembly and a high torque, electric stirring-motor with gear-reducers. It had a glass jacket to allow for either heating or cooling of the reactor contents utilizing a separate, water-circulating bath. An O-ring, which fit into grooves in the glass joint of the bottom and the steel top, sealed the reactor to prevent gas leaks.
- 30 Monomer mix was prepared by adding the following reagents to a beaker in the following order: 300.00 g acrylic acid, the amount of the desired crosslinker indicated in Table VIII, 0.75 g VERSENEX 80 (Trademark of The Dow Chemical Company) chelating agent, 1.50 g of a 5 percent solution of VINOL® 205 (Trademark of Air Products Company) polyvinyl alcohol in water (if necessary to help disperse a crosslinking agent not fully soluble in the monomer mix),
- 35 and 300 mL water. To the resulting solution was added a solution of 144.0 g sodium carbonate dissolved in 515 mL of water.

Monomer mix was loaded to the reactor through the loading tube that had a small ball valve for flow control. After monomer loading was complete, nitrogen gas was bubbled into the monomer solution to remove dissolved oxygen. After the desired sparging

time the free radical initiator solutions were added through the dip-tube opening in the reactor top, by syringe: 4.8 mL of a 10 percent solution of sodium persulfate in water, followed by 1.2 mL of a 10 percent solution of sodium erythorbate in water. A very slight nitrogen pressure was maintained in the reactor during initiator addition to prevent air from entering the reactor through the opening.

Typical Monomer Mix

Recipe value

300.00 g acrylic acid
crosslinking agent

24.8 wt. %
varies

0.75 g VERSENEX 80 chelating agent

2500 ppm BOM*

1.50 g of a 5% solution of Vinol 205
polyvinylalcohol in water

250 ppm BOM

300 mL water

144.0 g sodium carbonate dissolved in
515 mL of water (21.9%)

65.2 mol %
neut.

4.8 mL of a 10% solution of sodium
persulfate in water

1600 ppm BOM

1.2 mL of a 10% solution of sodium
erythorbate

400 ppm BOM

*Based on monomer

Within a few minutes, an exothermic polymerization began. The temperature of the reaction mixture rose to 80°C over a 40 minute period, and was then decreased to 65°C and maintained there for three hours by means of the circulating bath. The crumbly, rubber-like gel product was removed from the reactor, spread onto a nylon screen and dried in a 100°C oven for 16 hours. The dried polymer was cooled and then pulverized in a food blender. The amount of extractables, centrifuged swelling capacity, swollen modulus, and the AUL were measured on these samples.

The polymer powder thus made was placed in a flat-bottomed, glass crystallizing dish. The dish was put into a forced air oven that was maintained at 200°C to achieve a heat-treatment separate from the mild drying step. Samples were withdrawn at various times and their properties were determined. The mass-loss upon heating for many of the polymers was also measured. In these instances, individual dishes were prepared for treatment. The change in mass was measured as a function of heating time and the percentage loss was calculated. The mass loss at 200°C averaged about 6 percent for samples initially dried at 100°C for 16 hours. Thermal analysis (thermogravimetry coupled with gas chromatography and mass spectrometry) showed this mass was water. Traces of carbon dioxide were detected in the thermal analysis at higher temperatures.

The differences between products made with different crosslinking agents became apparent after the heat-treatment of the dried polymer. In Table VIII below are given

data on the physical properties of the polymers before and after heating at 200°C for 120 minutes:

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Table VIII. Results from Representative Polymerizations with Various Crosslinking Agents

Sample crosslinked with:	Concentration of Crosslinking Agent ¹	Centrifuge Capacity (g/g)	AUL ² (g/g)	Modulus (dyne/cm ²)	Extractable Polymer
METHYLENEBISACRYLAMIDE before heating	0.5	27.8	26.4	50900	0.5
after heating		33.8	31.4	43200	1.5
BISACRYLAMIDOACETIC ACID before heating	0.65	30	25.8	50300	1.7
after heating		33.3	32.7	47600	2.4
ALLYLMETHACRYLATE before heating	0.65	24.8	27.6	41100	2.4
after heating		32.0	30.4	43500	3.6
ALLYLACRYLATE before heating	0.8	30.6	29.0	33600	2.1
after heating		34.5	30.7	33500	3.7

¹ Parts based on 100 parts of the α,β -ethylenically unsaturated monomer.

² Absorbency Under Load in 60 minutes under 0.3 psi load

Example 7: Comparison of Different Heat Treatment Temperatures and Times on Absorptive Properties when a Preferred Crosslinking Agent is Employed

A mixture of 15 grams VINOL V-205 (available from Air Products Corp.) in 250 grams deionized water was heated to form a solution. In a separate flask, 300 grams acrylic acid, 2.1 grams allylmethacrylate, 0.75 grams VERSENEX 80 chelating agent (available from the Dow Chemical Company) and 70 grams deionized water were mixed to form a clear monomer mixture. The clear monomer mixture was neutralized with a solution of 144 grams sodium carbonate in 450 grams deionized water to form a neutralized monomer mixture. The neutralized monomer mixture was charged into a 2 liter reactor, which was then purged with nitrogen for 45 minutes. The polymerization was initiated with a mixture of 4.8 mL of a 10% aqueous solution of sodium persulfate, 0.6 mL of a 10% aqueous solution of sodium erythorbate, and 0.5 mL of a 30% aqueous solution of hydrogen peroxide. Within a few minutes, an exothermic polymerization began. The temperature of the reaction mixture rose to 80°C over a 40 minute period, and was then decreased to 65°C and maintained there for three hours by means of a circulating bath. The crumbly, rubber-like gel product was removed from the reactor, spread onto a nylon screen and dried in a 100°C oven for 16 hours. The dried polymer was cooled and then pulverized in a food blender. The centrifuge capacity and the sixty minute 0.3 psi AUL were measured on these samples.

The polymer powder thus made was placed in a flat-bottomed, glass crystallizing dish. The dish was put into a forced air oven that was maintained at the indicated temperature for the indicated time to achieve a heat-treatment separate from the mild drying step. Samples were withdrawn at various times and their properties were determined. The data are set forth in the following Table IX.

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TABLE IX

Temperature of Heat Treatment (°C)	Time for Heat Treatment (minutes)	Centrifuge Capacity (g/g)	Sixty minute 0.3 psi AUL (g/g)
none	none	32.3	17.3
170	5	33.1	19.8
	15	32.2	24.8
	60	31.8	29.4
180	5	34.8	20.3
	15	34.2	28.4
	60	34.1	29.4
190	5	35.2	22.1
	15	35.4	28.4
	60	34.2	29.4
200	5	32.0	18.9
	15	32.4	28.6
	60	31.9	29.8
215	30	33.3	32.5
230	30	32.5	32.0

Example 8: Grafting

To illustrate the effect obtained when grafting polymers are included in the allyl methacrylate crosslinked polymerization recipe, the following gel polymerizations were carried out in a 30 gallon reactor using the process set forth in Example 6:

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<u>Recipe</u>	<u>A</u> <u>Non-</u> <u>Grafted</u>	<u>B</u> <u>Grafted</u>
Acrylic acid, pounds	46	50
Allyl methacrylate, grams	108	182
Poly(vinyl alcohol), pounds	0	2.5
VERSENEX 80 chelating agent, grams	52	30
Soda ash, pounds	22	23
Sodium Persulfate, grams	33.4	38.5
30% Hydrogen Peroxide, grams	34.8	40
Sodium erythorbate, grams	4.2	9.0
Water, total pounds added	107	125.5
Heat-treating air temperature (30 minutes), °C	170	200

RESULTS

Centrifuge capacity, g/g	30.6	32.0
Swollen modulus, dynes/cm ²	45,600	45,600
% extractable polyacrylate	4.8	ND
AUL, g/g at 0.3 psi for 60 min.	30.7	29.6

The above results show that the presence of poly(vinyl alcohol) as a graft substrate resulted in improved centrifuge capacity with only a slight decrease in absorbency under load and equivalent modulus to the product obtained using a non-grafted polymer.

20 While the subject invention has been described largely in terms of superabsorbent polymers prepared by a gel polymerization process, it is expected that superabsorbent polymers prepared by well-known suspension polymerization polymerizations could benefit equally from the disclosed heat treatments.

25 Various modifications may be made in the present invention without departing from the spirit or scope thereof as will be readily apparent to those skilled in the art.

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WHAT IS CLAIMED IS:

1. A process for producing a superabsorbent polymer comprising polymerizing at least one α,β -ethylenically unsaturated monomer in an aqueous phase in the presence of a suitable initiator and a crosslinking agent and thereafter drying the polymer at a temperature between about 100°C and about 180°C to form a dried polymer, characterized in that the process further comprises heating the dried polymer in the absence of a surface crosslinking agent to a temperature between about 165°C and about 230°C for a time sufficient to produce a heat-treated polymer having a sixty minute 0.3 psi AUL of at least about 25 grams/gram.
2. The process of Claim 1, wherein the α,β -ethylenically unsaturated monomer is selected from the group consisting of acrylic acid, methacrylic acid, and alkali metal salts of said acids.
3. The process of Claim 1, wherein said crosslinking agent is selected from the group consisting of trimethylolpropanetriacrylate, butyleneglycoldiacrylate, ethyleneglycoldimethacrylate, ethylenebisacrylamide, diallylcarbonate, methylenebisacrylamide, bis(acrylamido)acetic acid and its salts, allylacrylate, allylmethacrylate and esters or amides having both a vinyl and an allyl functionality.
4. The process of any of Claims 1, 2, or 3, wherein said crosslinking agent is employed in an amount of from about 0.0005 to about 5 parts by weight based on 100 parts by weight of said α,β -ethylenically unsaturated monomer.
5. The process of any of Claims 1, 2, or 3, wherein said crosslinking agent is employed in an amount of from about 0.1 to about 1 part by weight based on 100 parts by weight of said α,β -ethylenically unsaturated monomer.
6. The process of any of Claims 1, 2, or 3, wherein said heat-treated polymer is further characterized by a centrifuge capacity of at least about 26 grams/gram.
7. The process of any of Claims 1, 2, or 3, wherein said heat-treated polymer is further characterized by a 16 hour extractable level less than about 8 percent.

8. The process of any of Claims 1, 2, or 3, wherein said dried polymer is characterized by a centrifuge capacity greater than about 30 grams/gram and a sixty minute 0.3 psi AUL less than about 25 grams/gram, and wherein said heating increases the sixty minute 0.3 psi AUL to at least about 25 grams/gram, without decreasing the centrifuge capacity to less than about 29 grams/gram.

9. The process of any of Claims 1, 2, or 3, wherein said α,β -ethylenically unsaturated monomer is polymerized with between 1 and 5 percent by weight of a C_1 to C_6 acrylate or methacrylate based on the weight of the α,β -ethylenically unsaturated monomer, wherein said dried polymer is characterized by a sixty minute 0.3 psi AUL of at least about 26, and wherein said heat-treated polymer is characterized by a sixty minute AUL of at least about 28.

10. The process of Claim 9, wherein said C_1 to C_6 acrylate or methacrylate is methyl acrylate or methyl methacrylate.

11. The process of Claim 9, wherein said heat-treated polymer is further characterized by a 16 hour extractables level less than about 4 percent.

12. The process of Claim 1, wherein said crosslinking agent is selected from the group consisting of methylenebisacrylamide, bis(acrylamido)acetic acid and its salts, allyl acrylate, allylmethacrylate and difunctional monovinyl and monoallyl esters and amides.

13. The process of Claim 12, wherein said crosslinking agent is allyl methacrylate.

14. The process of Claim 12, wherein said crosslinking agent is methylenebisacrylamide.

15. The process of Claim 12, wherein said crosslinking agent is bis(acrylamido)acetic acid or its salts.

16. The process of Claim 12, wherein said heat-treated polymer is characterized by a 60 minute 0.3 psi AUL of at least about 30 grams/gram.

17. The process of Claim 12, wherein said heat-treated polymer is characterized by a 60 minute 0.3 psi AUL of at least about 30 grams/gram, a centrifuge capacity of at least about 30 grams/gram, and a 16 hour extractables level less than about 5 percent.

18. The process of Claim 12, wherein said heat-treated polymer is characterized by a 60 minute 0.3 psi AUL of at least about 30 grams/gram, a centrifuge capacity of at least about 32 grams/gram, and a 16 hour extractables level less than about 4 percent.

19. The process of any of Claims 12, 16, 17, or 18, wherein said dried polymer is characterized by a 60 minute 0.3 psi AUL of at least about 25 grams/gram.

20. A superabsorbent polymer comprising polymerized moieties of at least one α,β -ethylenically unsaturated monomer and at least one crosslinking agent, said polymer being characterized by a 60 minute 0.3 psi AUL of at least about 30 grams/gram, a centrifuge capacity of at least about 32 grams/gram, and a 16 hour extractables level less than about 4 percent.

21. A superabsorbent polymer comprising polymerized moieties of at least one α,β -ethylenically unsaturated monomer and at least one crosslinking agent, wherein said crosslinking agent is selected from the group consisting of methylenebisacrylamide, bis(acrylamido)-acetic acid and its salt, allyl acrylate, allylmethacrylate and difunctional monovinyl and monoallyl esters and amides.

22. A method of using the superabsorbent polymer of either Claim 20 or 21 comprising retaining said polymer in conjunction with hydrophilic fibers in an absorbent structure.

23. The method of Claim 24, wherein said absorbent structure is further retained within a disposable diaper, a sanitary napkin, or an incontinence device.

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INTERNATIONAL SEARCH REPORT

- International Application No

PCT/US 92/07611

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁴ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 08 F 6/00, C 08 F 220/06, A 61 L 15/24														
II. FIELDS SEARCHED <div style="text-align: center; font-size: small;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 25%; border: none; vertical-align: top;">Classification System</td> <td style="border: none; vertical-align: top;">Classification Symbols</td> </tr> <tr> <td style="border: none; vertical-align: top;">IPC⁵</td> <td style="border: none; vertical-align: top;">A 61 L 15/00, C 08 F 6/00, C 08 F 20/00, C 08 F 220/00</td> </tr> </table> <div style="text-align: center; font-size: x-small; margin-top: 5px;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC ⁵	A 61 L 15/00, C 08 F 6/00, C 08 F 20/00, C 08 F 220/00								
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IPC ⁵	A 61 L 15/00, C 08 F 6/00, C 08 F 20/00, C 08 F 220/00													
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse; font-size: x-small;"> <thead> <tr> <th style="width: 10%;">Category ¹⁰</th> <th style="width: 70%;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td style="vertical-align: top;">US, A, 4 286 082 (TSUBAKIMOTO et al.) 25 August 1981 (25.08.81), see claims 1,6,7,9; examples (cited in the application). ---</td> <td style="vertical-align: top; text-align: center;">1-6, 12, 14, 21-23</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td style="vertical-align: top;">DE, A1, 3 609 545 (BASF AG) 24 September 1987 (24.09.87), see claims 1,4; column 3, lines 55-60. ---</td> <td style="vertical-align: top; text-align: center;">1-5, 10, 12, 14, 21</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td style="vertical-align: top;">EP, A2, Q 289 338 (NIPPON SHOKUBAI KAGAKU KOGYO CO., LTD) 02 November 1988 (02.11.88), see claim 1; examples. -----</td> <td style="vertical-align: top; text-align: center;">1-5, 12, 14, 21</td> </tr> </tbody> </table>			Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	US, A, 4 286 082 (TSUBAKIMOTO et al.) 25 August 1981 (25.08.81), see claims 1,6,7,9; examples (cited in the application). ---	1-6, 12, 14, 21-23	A	DE, A1, 3 609 545 (BASF AG) 24 September 1987 (24.09.87), see claims 1,4; column 3, lines 55-60. ---	1-5, 10, 12, 14, 21	A	EP, A2, Q 289 338 (NIPPON SHOKUBAI KAGAKU KOGYO CO., LTD) 02 November 1988 (02.11.88), see claim 1; examples. -----	1-5, 12, 14, 21
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<div style="display: flex; justify-content: space-between; font-size: x-small;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁴</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means ⁴</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 50%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p> </div> </div>														
IV. CERTIFICATION <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> Date of the Actual Completion of the International Search <div style="text-align: center; font-size: large;">16 November 1992</div> </td> <td style="width: 50%; border: none; vertical-align: top;"> Date of Mailing of this International Search Report <div style="text-align: center; font-size: large;">25 NOV 1992</div> </td> </tr> <tr> <td style="width: 50%; border: none; vertical-align: top;"> International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="width: 50%; border: none; vertical-align: top;"> Signature of Authorized Officer <div style="text-align: center;">PUSTERER e.h.</div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center; font-size: large;">16 November 1992</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-size: large;">25 NOV 1992</div>	International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center;">PUSTERER e.h.</div>								
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ANHANG

ANNEX

ANNEXE

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

to the International Search
Report to the International Patent
Application No.

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/US 92/07611 SAE 64563

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angeführten Patentedokumente angegeben.
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cited in the above-mentioned inter-
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US A 4286082	25-08-81	JP A2 56091837 JP B4 58025500 JP A2 55133413 JP B4 61036763	25-07-81 27-05-83 17-10-80 20-08-86
DE A1 3609545	24-09-87	AT E 46913 AU A1 70427787 AU B2 590693 CA A1 1282200 DE C0 3760674 EP A2 238050 EP A3 238050 EP B1 238050 JP A2 62227904 US A 4873299	15-10-89 24-09-87 09-11-89 26-03-91 09-11-89 23-09-87 25-11-87 04-10-89 06-10-87 10-10-89
EP A2 289338	02-11-88	CN A 88103323 CN B 1015180 DE C0 3865509 EP A3 289338 EP B1 289338 ES T3 2026653 US A 4920202 JP A2 1026604	21-12-88 25-12-91 21-11-91 12-04-89 16-10-91 01-05-92 24-04-90 27-01-89

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